

Supporting Information

Side-chain shuffling: Regioselective synthesis of mixed tail discotic mesogens

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Materials and methods

NMR spectra were obtained using either a Varian Inova spectrometer at 500 MHz (^1H) and 125 MHz (^{13}C); or a Bruker Avance 600 MHz (^1H) and 150 MHz (^{13}C) or 400 MHz (^1H) and 100 MHz (^{13}C), as specified. EI mass spectrometry was performed using either a Varian 4000 GC/MS/MS equipped with a direct probe and ionization energy of 70 eV or a Hewlett-Packard 5985 mass spectrometer with EI of 70 eV by Simon Wong and Hongwen Chen (Simon Fraser University), as specified. MALDI-TOF experiments were performed on a Perspective Voyager-DE STR from PE Applied Biosystems using a nitrogen laser (337 nm) to desorb the analytes from the 2,5-dihydroxybenzoic acid matrix. High Resolution Mass Spectrometry (HR-MS) was performed on an Agilent 6210 TOF LC-MS with electrospray ionization (ESI).

Elemental analysis was obtained from Mr. Miki Yang and Mr. Frank Haftbaradaran at Simon Fraser University using a EA1110 CHN CE Instrument with WO_3 as an accelerant. The analysis was performed on a small amount of product that was vacuum-

dried for about 24 hours. FT-IR spectra were recorded on a Thermo-Nicolet Nexus 670 FT-IR E.S.P. spectrometer using dried KBr pellets.

Melting points were measured on a Melt-Temp II apparatus from Laboratories Devices without correction or calibration using a mercury thermometer (-10 to 300 °C). DSC analysis was performed on a Perkin Elmer DSC 7 and the values for the temperatures and enthalpies of transition were recorded on the first heating/cooling cycle at a rate of 5 °C/min. Polarized optical microscopy was carried out using an Olympus BX50 polarized optical microscope equipped with a Linkam LTS350 heating stage.

Variable temperature X-ray diffraction experiments were performed using Rigaku RAXIS rapid diffractometer with a Cu K α radiation, a graphite monochromator and a Fujifilm Co. Ltd. Curved image plate (460 mm x 256 mm). Samples were loaded into capillaries (~1 mm diameter) from the isotropic phase and the temperature was controlled using a home-made capillary furnace.¹

All chemicals were used as purchased, unless otherwise noted. Dichloromethane was dried by distillation over CaCl₂ and dimethylformamide was dried over 4 Å molecular sieves. Other solvents were used without further purification. Nitrogen gas was purchased from Praxair. Silica (230-400 mesh) and TLC plates were obtained from Silicycle Inc. Deuterated solvents (CDCl₃ and DMSO-d₆) were purchased from Aldrich. 1-Bromohexane, 1-bromooctane, 1-bromodecane, ICl, LiOH-H₂O, BF₃•Et₂O, VOF₃, SnCl₂, H₂O₂, BBr₃, NBu₄Br, butanone, (*i*-Pr)₂NH, CuI, sulfuric acid, 2,3-diaminomaleonitrile, HNO₃, veratrole, catechol, FeCl₃, I₂ and HBr were purchased from Aldrich. DMF, THF, DCM, hexanes, ethyl acetate, DMSO, pyridine were purchased from VWR. Citric acid,

K₂CO₃, Na₂SO₃, NaCl, MgSO₄, NaHCO₃, NaOAc, Na₂S₂O₃, methanol, acetic acid, HCl and acetic anhydride were purchased from Caledon Laboratories Ltd.. TMS-Acetylene, Pd(PPh₃)₄ and PdCl₂(PPh₃)₂ were obtained from Strem Chemicals Inc. 1,2-phenylenediamine was purchased from Eastman Kodak. Ethanol was obtained from Commercial Alcohols Inc..

2-Hexyloxyphenyl acetate (3a)² Catechol (10.00 g, 90.8 mmol), bromohexane (15.00 g, 90.8 mmol, 12.8 mL) and tetrabutylammonium bromide (1.46 g, 4.54 mmol) were mixed in butanone and nitrogen was bubbled through the solution for ten minutes. K₂CO₃ (25.10 g, 180 mmol) was added and the solution was purged for an additional five minutes before being heated at reflux for 24 hours. The progress of the reaction was followed by TLC (hexanes/ethyl acetate, 96:4) until completion. The mixture was cooled to room temperature, water (150 mL) was added and the phases separated. The organic layer was washed with water (150 mL) twice and then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was purified over silica (hexanes/ethyl acetate: 96/4) to yield 2-hexyloxyphenol as a light yellow oil (9.12 g, 47.0 mmol, 52 %). ¹H NMR (CDCl₃) δ 0.90-0.93 (m, 3H), 1.33-1.37 (m, 4H), 1.44-1.47 (m, 2H), 1.82 (q, 2H, *J* = 7.1 Hz), 4.04 (t, 2H, *J* = 6.5 Hz), 5.65 (s, 1H), 6.81-6.88 (m, 3H), 6.92-6.94 (m, 1H); MS-CI for [C₁₂H₁₈O₂-H]⁺ calculated (found): 195.1 (195.1).

2-Hexyloxyphenol (7.00 g, 36.1 mmol), pyridine (15 mL) and acetic anhydride (15 mL) were mixed and the mixture was heated at reflux overnight. The solution was cooled to room temperature, water was added and the solution was cooled in a water bath for 20 minutes. The aqueous phase was extracted with three portions of dichloromethane (75

mL) and the organic phases were combined. The organic phase was washed with $\text{HCl}_{(\text{aq})}$ 10 % until the aqueous phase remained acidic, then with water (150 mL) and brine (150 mL). The solution was dried over MgSO_4 , filtered and evaporated to yield a brownish oil (7.97 g, 33.8 mmol, 94 %) that was used without further purification. ^1H NMR (CDCl_3) δ 0.89-0.92 (m, 3H), 1.31-1.36 (m, 4H), 1.41-1.46 (m, 2H), 1.76 (quint, 2H, $J = 7.0$ Hz), 2.30 (s, 3H), 3.97 (t, 2H, $J = 6.5$ Hz), 6.91-6.96 (m, 2H), 7.03 (dd, 1H, $J = 7.8, 1.5$ Hz), 7.46 (dd, 1H, $J = 7.8, 1.5$ Hz); MS-CI for $[\text{C}_{14}\text{H}_{20}\text{O}_3\text{-H}]^+$ calculated (found): 237.1 (237.1).

2-Hexyloxy-5-iodophenyl acetate (4a) 2-(Hexyloxy)phenyl acetate (5.27 g, 22.3 mmol) was dissolved in dichloromethane (40 mL) and cooled in an ice/water bath. A solution of iodine monochloride (ICl , 3.98 g, 24.5 mmol, 1.23 mL) in dichloromethane (25 mL) was added slowly to the reaction mixture, which was then allowed to warm to room temperature and stirred at room temperature for 3 hours. The solution was poured over cold $\text{Na}_2\text{S}_2\text{O}_3$ (sat) (100 mL) and stirred until the red color disappeared. The phases were separated and the aqueous phase was extracted twice with dichloromethane (50 mL). The organic phases were combined and washed with water (150 mL) twice and then brine (150 mL). The solution was dried over MgSO_4 , filtered and evaporated to yield as a yellow oil (7.28 g, 20.1 mmol, 90 %) which was used without further purification. ^1H NMR (500 MHz, CDCl_3) δ 0.90 (t, 3H, $J = 7$ Hz), 1.31-1.35 (m, 2H), 1.38-1.44 (m, 4H), 1.74 (quint, 2H, $J = 7.1$ Hz), 2.28 (s, 3H), 3.94 (t, 2H, $J = 6.5$ Hz), 6.70 (d, 1H, $J = 8.5$ Hz), 7.33 (d, 1H, $J = 2$ Hz), 7.46 (dd, 1H, $J = 8.5, 2$ Hz); MS-CI for $[\text{C}_{14}\text{H}_{19}\text{IO}_3\text{-H}]^+$ calculated (found): 363.0 (363.0).

2-Decyloxy-1-hexyloxy-4-iodobenzene (5a) 2-Hexyloxy-5-iodophenyl acetate (7.20 g, 19.9 mmol) was dissolved in methanol (25 mL), THF (25 mL) and H₂O (10) and LiOH•H₂O (2.62 g, 62.5 mmol) was added in one portion. The mixture was allowed to stir at room temperature for four hours. The solution was poured over cold 10 % HCl (aq) to obtain a solution having pH lower than seven and the aqueous phase was extracted with three portions of DCM (150 mL). The organic phases were combined and washed with water (200 mL) and then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated to yield 2-hexyloxy-5-iodophenol as a pale brown oil (6.11 g, 19.1 mmol, 96 %) that was used without further purification. ¹H NMR (500 MHz, CDCl₃) δ 0.89-0.92 (m, 3H), 1.32-1.35 (m, 4H), 1.43-1.46 (m, 2H), 1.80 (quint, 2H, *J* = 7.1 Hz), 4.00 (t, 2H, *J* = 6.8 Hz), 5.61 (s, 1H), 6.58 (d, 1H, *J* = 8.5 Hz), 7.13 (dd, 1H, *J* = 8.5, 2 Hz), 7.23 (d, 1H, *J* = 2 Hz); MS-Cl for [C₁₂H₁₇IO₂] calculated (found): 320.0 (320.0).

2-Hexyloxy-5-iodophenol (6.11 g, 19.1 mmol), bromodecane (4.65 g, 21.0 mmol, 4.35 mL) and tetrabutylammonium bromide (0.50 g, 1.55 mmol) were mixed in butanone (90 mL) and nitrogen was bubbled through the solution for ten minutes. K₂CO₃ (7.65 g, 55.4 mmol) was added and nitrogen was bubbled for another five minutes before heating the reaction mixture at reflux overnight. The mixture was cooled to room temperature, water and CH₂Cl₂ were added (50 mL each) and the phases were separated. The aqueous phase was extracted twice with DCM (75 mL), the organic phases were combined and the solution was washed with water (200 mL) and then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated to yield a white solid that was recrystallised

from EtOH (7.06 g, 15.3 mmol, 80 %). mp 40-41 °C; ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.91 (m, 6H), 1.27-1.35 (m, 16H), 1.42-1.48 (m, 4H), 1.76-1.83 (m, 4H), 3.93-3.96 (m, 4H), 6.61 (d, 1H, *J* = 8.5 Hz), 7.12 (d, 1H, *J* = 2Hz), 7.17 (dd, 1H, *J* = 8.5, 2 Hz); ¹³C NMR (125 MHz, CDCl₃) δ 14.00, 14.09, 22.58, 22.65, 25.63, 25.95, 29.12, 29.14, 29.24, 29.31, 31.55, 31.79, 69.32, 69.39, 82.48, 115.66, 122.60, 129.77, 149.20, 150.10 (2 carbon signals missing/overlapping); MS-CI for [C₂₂H₃₇IO₂-H]⁺ calculated (found): 461.2 (460.9); Elemental Analysis (%) for [C₂₂H₃₇IO₂] calculated (found): C, 57.39 (57.58); H, 8.10 (8.08).

2-Decyloxyphenyl acetate (3b) Catechol (5.00 g, 45.4 mmol), NBu₄Br (0.305 g, 0.946 mmol) and bromodecane (8.37 g, 37.8 mmol, 7.8 mL) were dissolved in butanone (200 mL) and N₂ was bubbled through the solution for 15 minutes. K₂CO₃ (5.18 g, 37.5 mmol) was added and the solution was purged for another ten minutes prior to be heated at reflux overnight. The solution was cooled to room temperature and HCl (20 %) was added until the effervescence stopped. Dichloromethane (150 mL) was added and the two phases were separated. The aqueous phase was extracted twice with DCM (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The product, 2-decyloxyphenol, was purified over silica (hexanes/ethyl acetate: 96/4) to yield a clear oil (2.76 g, 11.0 mmol, 29 %). ¹H NMR (500 MHz, CDCl₃) δ 0.89 (t, 3 H, *J* = 7 Hz), 1.28-1.39 (m, 12 H), 1.43-1.49 (m, 2 H), 1.79-1.84 (m, 2H), 4.03 (t, 2H, *J* = 6.8 Hz), 5.65 (s, 1H), 6.83-6.88 (m, 3H), 6.92-6.94 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 14.10, 22.66, 26.01, 29.24, 29.29, 29.36, 29.53, 29.55, 31.87, 68.87, 111.58, 114.39,

120.05, 121.26, 145.79, 145.95; MS-EI for [C₁₆H₂₆O₂] calculated (found): 250.2 (250.2); HR-MS for [C₁₆H₂₆O₂-H]⁺ calculated (found): 251.2007 (251.2011).³

2-Decyloxyphenol (2.17 g, 8.70 mmol) was suspended in acetic anhydride (5 mL), pyridine (5 mL) and heated at reflux overnight. The mixture was cooled to room temperature, water (100 mL) was added and the solution was cooled in a room temperature water bath. The aqueous solution was extracted three times with CH₂Cl₂ (75 mL) and the phases were combined. The organic layer was washed with large amounts of water (400 mL) twice, then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated to yield an amber oil (2.43 g, 8.31 mmol, 96%) that was used without further purification. ¹H NMR (CDCl₃, 600 MHz) δ 0.90 (t, 3H, *J* = 7.2 Hz), 1.29-1.39 (m, 12H), 1.41-1.46 (m, 2H), 1.74-1.79 (m, 2H), 2.31 (s, 3H), 3.97 (t, 2H, *J* = 6.3 Hz), 6.91-6.97 (m, 2H), 7.03 (dd, 1H, *J* = 7.8, 1.8 Hz), 7.18 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 14.10, 20.59, 22.67, 25.90, 29.18, 29.31, 29.33, 29.54, 29.58, 31.89, 68.63, 113.40, 120.56, 122.66, 126.78, 140.06, 150.60, 169.03; MS-EI for [C₁₈H₂₈O₃] calculated (found): 292.2 (292.1); HR-MS for [C₁₈H₂₈O₃-H]⁺ calculated (found): 293.2116 (293.2119).

2-Decyloxy-5-iodophenyl acetate (4b) 2-Decyloxyphenyl acetate (2.11 g, 7.22 mmol) was dissolved in CH₂Cl₂ (15 mL) and the solution was cooled with an ice bath. A mixture of iodine monochloride (ICl, 1.29 g, 7.96 mmol, 0.4 mL) in CH₂Cl₂ (10 mL) was added using a dropping funnel over about 30 minutes. The solution was allowed to warm to room temperature overnight. The reaction mixture was poured over a cold saturated solution of Na₂S₂O₃ (100 mL) and stirred until the red color disappeared. The phases

were separated and the aqueous phase was extracted twice with CH₂Cl₂ (75 mL). The organic phases were combined and washed with water (200 mL) then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated to yield a yellow oil that was used without further purification (2.93 g, 7.00 mmol, 97 %). ¹H NMR (CDCl₃, 600 MHz) δ 0.88 (t, 3H, *J* = 7.2 Hz), 1.27-1.34 (m, 12H), 1.38-1.45 (m, 2H), 1.72-1.76 (m, 2H), 2.05 (s, 3H), 3.93 (t, 2H, *J* = 6.3 Hz), 6.70 (d, 1H, *J* = 8.4 Hz), 7.33 (d, 1H, *J* = 2.4 Hz), 7.46 (dd, 1 H, *J* = 8.4, 2.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 14.10, 20.44, 22.66, 25.82, 29.02, 29.28, 29.30, 29.52, 29.55, 31.88, 68.81, 81.04, 115.20, 131.46, 135.60, 140.74, 150.81, 168.55; MS-EI for [C₁₈H₂₇IO₃] calculated (found): 418.1 (418.1) ; HR-MS found for [C₁₈H₂₇IO₃-H]⁺ calculated (found): 419.1083 (419.1076).

2-Decyloxy-5-iodophenol (5b) 2-Decyloxy-5-iodophenyl acetate (2.77 g, 6.62 mmol) was dissolved in a mixture of MeOH (10 mL), THF (10 mL) and H₂O (5 mL). LiOH•H₂O (0.97 g, 23 mmol) was added in one portion and the mixture was stirred at room temperature overnight. HCl (20%) was added until the pH was acidic and the aqueous solution was extracted three times with CH₂Cl₂ (75mL). The organic layers were combined and washed with water (200 mL) then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated to yield 2-decyloxy-5-iodophenol as a yellow oil that was used without further purification (2.01 g, 5.35 mmol, 81 %). ¹H NMR (CDCl₃, 600 MHz) δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.27-1.37 (m, 12 H), 1.41-1.47 (m, 2H), 1.77-1.82 (m, 2H), 4.0 (t, 2H, *J* = 6.6 Hz), 5.6 (s, 1H), 6.58 (d, 1H, *J* = 8.4 Hz), 7.13 (dd, 1H, *J* = 8.4, 2.4 Hz), 7.23 (d, 1H, *J* = 2.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 14.10, 22.66, 25.93, 29.07, 29.28, 29.31, 29.51, 29.55, 31.86, 69.06, 82.75, 113.34, 123.32, 128.96, 146.03,

146.71; MS-EI for $[C_{16}H_{25}IO_2]$ calculated (found) 376.1 (376.1); HR-MS for $[C_{16}H_{25}IO_2-H]^+$ calculated (found): 377.0977 (377.0977).

2-Decyloxy-5-iodophenol (6.11 g, 16.2 mmol), NBu_4Br (0.262 g, 0.813 mmol) and bromohexane (4.02g, 24.3 mmol, 3.4 mL) were dissolved in butanone (200 mL) and N_2 was bubbled through the solution for 15 minutes. K_2CO_3 (6.73 g, 48.7 mmol) was added and the solution was purged for another ten minutes prior to being heated at reflux overnight. The solution was cooled to room temperature and 20 % HCl was added until the effervescence stopped. Dichloromethane (100 mL) was added and the two phases were separated. The aqueous phase was extracted twice with CH_2Cl_2 (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) then brine (200 mL). The solution was dried over $MgSO_4$, filtered and evaporated. The solid was recrystallized with ethanol, filtered and air-dried to yield a white solid (5.38 g, 11.7 mmol, 72 %). mp: 38-40 °C; 1H NMR ($CDCl_3$, 600 MHz) δ 0.87-0.92 (m, 6H), 1.26-1.36 (m, 16H), 1.42-1.49 (m, 4H), 1.76-1.82 (m, 4H), 3.95 (t, 4H, $J = 6.6$ Hz), 6.61 (d, 1H, $J = 8.4$ Hz), 7.12 (d, 1H, $J = 1.8$ Hz), 7.18 (dd, 1H, $J = 8.4, 1.8$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.01, 14.10, 22.59, 22.68, 25.63, 25.97, 29.11, 29.17, 29.33, 29.38, 29.55, 29.59, 31.53, 31.89, 69.33, 69.40, 82.48, 115.67, 122.61, 129.78, 149.22, 150.11; MS-EI for $[C_{22}H_{37}O_2I]$ calculated (found): 460.2 (460.3); HR-MS for $[C_{22}H_{37}IO_2-H]^+$ calculated (found): 461.1916 (461.1911).

3-Decyloxy-1-ethynyl-4-hexyloxybenzene (6a) 2-Decyloxy-1-hexyloxy-4-iodobenzene (**5a**) (4.00 g, 8.69 mmol), CuI (0.497 g, 2.61 mmol) and $PdCl_2(PPh_3)_2$ (0.153, 0.217 mmol) were mixed in a round bottom flask and submitted to three cycles of vacuum/ N_2 .

(*i*-Pr)₂NH (85 mL) and TMS-Acetylene (10.2 g, 104 mmol, 14.7 mL) were added to the solids and N₂ was bubbled for 15 minutes. The reaction mixture was heated at 60 °C for 24 hours, and then cooled to room temperature. H₂O and HCl_(conc.) were added until the pH was acidic. The aqueous phase was extracted with CH₂Cl₂ (100 mL) three times and the organic phases were combined, washed with water (200 mL) and brine (200 mL). The organic phase was dried over MgSO₄, filtered and evaporated. The crude black oil was purified over silica (hexanes/ethyl acetate: 96:4) to yield 2-(3-Decyloxy-4-hexyloxyphenyl)ethynyltrimethylsilane as a pale brown oil that was used without further purification (3.30 g, 7.66 mmol, 88 %). ¹H NMR (500 MHz, CDCl₃) δ 0.24 (s, 9H), 0.87-0.91 (m, 6H), 1.27-1.36 (m, 16H), 1.42-1.48 (m, 4H), 1.81 (quint., 4 H, *J* = 7.1 Hz), 3.96-3.99 (m, 4H), 6.76 (d, 1H, *J* = 8 Hz), 6.96 (d, 1H, *J* = 2Hz), 7.03 (dd, 1H, *J* = 8, 2 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 0.06, 14.01, 14.11, 22.59, 22.68, 25.64, 25.99, 29.12, 29.20, 29.33, 29.38, 29.56, 29.60, 31.57, 31.90, 69.07, 69.17, 92.04, 105.47, 112.98, 115.12, 116.88, 125.40, 148.53, 149.83; MS-CI for [C₂₇H₄₆O₂Si-H]⁺ calculated (found): 431.5 (431.3); HR-MS for [C₂₇H₄₆O₂Si-H]⁺ calculated (found): 431.3345 (431.3343).

2-(3-Decyloxy-4-hexyloxyphenyl)ethynyltrimethylsilane (3.13 g, 7.69 mmol) was dissolved in MeOH (45 mL) and THF (45 mL). K₂CO₃ (2.66 g, 19.2 mmol) was added and the mixture was stirred at room temperature for three hours and TLC (hexanes 100 %) indicated total conversion of the starting material. The reaction mixture was poured over silica, washed with DCM and evaporated to yield a dark brown oil that was used without further purification in the next step (2.65 g, 7.39 mmol, 74 %). ¹H NMR (500 MHz, CDCl₃) δ 0.87-0.92 (m, 6H), 1.27-1.36 (m, 16H), 1.43-1.49 (m, 4H), 1.79-1.83 (m, 4H), 2.98 (s, 1H), 3.96-4.00 (m, 4H), 6.79 (d, 1H, *J* = 8.5 Hz), 6.99 (d, 1H, *J* = 2 Hz),

7.06 (dd, 1H, $J = 8.5, 2$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 14.1, 22.66, 22.68, 26.10, 26.04, 29.24, 29.29, 29.33, 29.35, 29.36, 29.53, 29.55, 31.87, 31.91, 68.87, 69.27, 111.58, 114.09, 114.39, 120.05, 120.98, 121.26, 145.79, 145.95; MS-Cl for $[\text{C}_{24}\text{H}_{38}\text{O}_2]$ calculated (found): 358.3 (358.4); HR-MS for $[\text{C}_{24}\text{H}_{38}\text{O}_2\text{-H}]^+$ calculated (found): 359.2950 (359.2941).

1-Decyloxy-4-ethynyl-2-hexyloxybenzene (6b) 4-Decyloxy-3-hexyloxyiodobenzene (**5b**) (3.62 g, 7.86 mmol), trimethylsilaneacetylene (7.47 g, 76.0 mmol, 10.7 mL) and (*i*-Pr) $_2$ NH (19.2 g, 190 mmol, 27 mL) were mixed in THF (100 mL). N_2 was bubbled through for ten minutes at room temperature. CuI (0.435 g, 2.29 mmol) and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.133 g, 0.190 mmol) were added and the solution was purged with N_2 for another ten minutes. The solution was stirred at room temperature for one hour, and then heated at 80 $^\circ\text{C}$ for 24 hours. The mixture was cooled to room temperature and poured onto a short silica column that was then washed with DCM. The organic phase was washed twice with water (150 mL), then brine (200 mL). The solution was dried over MgSO_4 , filtered and evaporated. The product was purified by column chromatography (hexanes/ethyl acetate; 98/2) to yield 4-trimethylsilaneethynyl-1-decyloxy-2-hexyloxybenzene as a brown oil (3.34 g, 7.75 mmol, 98 %). ^1H NMR (CDCl_3 , 600 MHz) δ 0.18 (s, 9H), 0.78-0.90 (m, 6H), 1.17-1.55 (m, 20 H), 1.69-1.80 (m, 4H), 3.86-3.98 (m, 4H), 6.76 (d, 1H, $J = 8$ Hz), 6.96 (d, 1H, $J = 2$ Hz), 7.03 (dd, 1H, $J = 8, 2$ Hz); ^{13}C NMR (CDCl_3 , 150 MHz) δ 0.10, 14.05, 14.14, 22.64, 22.71, 25.69, 26.00, 29.18, 29.36, 29.43, 29.51, 29.58, 29.62, 31.59, 31.93, 69.10, 69.20, 92.08, 105.50, 113.00, 115.15, 116.90, 125.43, 148.56, 149.86; MS-

EI for $[C_{27}H_{46}O_2Si-H]^+$ calculated (found): 431.3 (431.5); HR-MS for $[C_{27}H_{46}O_2Si-H]^+$ calculated (found): 431.3345 (431.3347).

4-Trimethylsilaneethynyl-1-decyloxy-2-hexyloxybenzene (3.25 g, 7.55 mmol) was dissolved in MeOH (50 mL) and THF (50 mL). K_2CO_3 (2.61 g, 18.88 mmol) was added in one portion and the mixture was stirred at room temperature overnight and TLC (98/2, hexanes/Ethyl acetate) showed completion of the reaction. The mixture was filtered on silica and washed with DCM. The product was obtained as a brown oil (2.41 g, 6.71 mmol, 89 %) that was used as is in the next step. 1H NMR ($CDCl_3$, 600 MHz) δ 0.87-0.92 (m, 6H), 1.22-1.37 (m, 16H), 1.43-1.49 (m, 4H), 1.79-1.83 (m, 4H), 2.98 (s, 1H), 3.96-4.00 (m, 4H), 6.79 (d, 1H, $J = 7.8$ Hz), 6.99 (d, 1H, $J = 1.8$ Hz), 7.06 (dd, 1H, $J = 7.8, 1.8$ Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 14.00, 14.09, 22.59, 22.67, 25.65, 25.97, 29.12, 29.14, 29.32, 29.38, 29.54, 29.58, 31.55, 31.89, 69.08, 69.21, 83.96, 113.04, 114.01, 117.06, 125.48, 148.61, 150.04; MS-EI for $[C_{24}H_{38}O_2-H]^+$ calculated (found): 359.3 (359.3); HR-MS for $[C_{24}H_{38}O_2-H]^+$ calculated (found): 359.2950 (359.2946).

3,3'-Didecyloxy-4,4'-dihexyloxydiphenylacetylene 2-Decyloxy-4-ethynyl-1-hexyloxybenzene (**6a**) (1.21 g, 3.36 mmol), 2-decyloxy-1-hexyloxy-4-iodobenzene (**5a**) (1.70 g, 3.70 mmol) and CuI (0.194 g, 1.02 mmol) were placed in a round-bottom flask (250 mL) and subjected to three vacuum/nitrogen cycles. $Pd(PPh_3)_4$ (0.196 g, 0.170 mmol) was added, the flask was purged twice with nitrogen and (*i*-Pr) $_2$ NH (70 mL, previously degassed with N_2) was added. The mixture was stirred for 30 minutes at room temperature and then at reflux overnight. The solution was cooled to room temperature and $HCl_{(conc.)}$ was added until the pH of the solution was acidic. DCM (100 mL) was

added and the two phases were separated. The aqueous phase was extracted twice with DCM (75 mL) and the organic layers were combined. The organic phase was washed with water (200 mL) and then brine (200 mL). The solution was dried over MgSO_4 , filtered and evaporated. Column chromatography (hexanes/dichloromethane: 50/50) and recrystallization with hot hexanes afforded a beige solid (1.07 g, 1.55 mmol, 46 %). mp: 85-87 °C; ^1H NMR (150 MHz, CDCl_3) δ 0.87-0.92 (m, 12H), 1.24-1.38 (m, 32H), 1.44-1.51 (m, 8H), 1.82 (quint., 8H, $J = 7.1$ Hz), 3.98-4.02 (m, 8H), 6.81 (d, 2H, $J = 8.5$ Hz), 7.02 (d, 2H, $J = 2$ Hz), 7.07 (dd, 2H, $J = 8.5, 2$ Hz); ^{13}C NMR (125 MHz, CDCl_3) δ 14.01, 14.10, 22.60, 22.68, 25.66, 26.01, 29.15, 29.21, 29.34, 29.40, 29.56, 29.61, 31.58, 31.90, 69.13, 69.19, 87.94, 113.25, 115.61, 116.51, 124.70, 148.69, 149.42; MALDI-TOF for $[\text{C}_{46}\text{H}_{74}\text{O}_4\text{-H}]^+$ calculated (found) 691.57 (691.59). Elemental Analysis (%) for $[\text{C}_{46}\text{H}_{74}\text{O}_4]$ calculated (found): C, 79.95 (80.02); H, 10.79 (10.43).

3,3'-Didecyloxy-4,4'-dihexyloxybenzil

3,3'-Decyloxy-4,4'-

dihexyloxydiphenylacetylene (1.00 g, 1.45 mmol) and I_2 (0.735 g, 2.89 mmol) were dissolved in DMSO (40 mL) and the mixture was heated at reflux for three hours, then allowed to cool down to room temperature overnight. The mixture was poured over a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$ (300 mL) and stirred until the solution was cool and the red colour disappeared. The aqueous phase was extracted three times with DCM (75 mL) and the organic phases were combined. The organic phase was washed with large amounts of water (350 mL) three times and then with brine (200 mL). The solution was dried over MgSO_4 , filtered and evaporated. The solid was recrystallized in hot hexanes to yield a light yellow solid (1.03 g, 1.42 mmol, 98%). mp: 100 °C ^1H NMR (500 MHz, CDCl_3) δ 0.87-0.91 (m, 12H), 1.27-1.37 (m, 32H), 1.44-1.50 (m, 8H), 1.81-1.87 (m, 8H), 4.04-4.07

(m, 8H), 6.84 (d, 2H, $J = 8.5$ Hz), 7.43 (dd, 2H, $J = 8.5, 2$ Hz), 7.56 (d, 2H, $J = 2$ Hz); ^{13}C NMR (150 MHz, CDCl_3) δ 13.98, 14.08, 22.56, 22.65, 25.56, 25.63, 25.89, 25.96, 28.88, 29.02, 29.23, 29.30, 31.50, 31.79, 69.10, 69.20, 111.55, 112.23, 126.11, 126.16, 149.27, 154.96, 193.81; MALDI-TOF for $[\text{C}_{46}\text{H}_{74}\text{O}_6]$ calculated (found): 722.55 (722.65); Elemental Analysis (%) for $[\text{C}_{46}\text{H}_{74}\text{O}_6]$ calculated (found): C, 76.41 (76.78); H, 10.32 (10.24).

2,7-Didecyloxy-3,6-dihexyloxyphenanthrene-9,10-dione In a dry two-necked round-bottom flask, 3,3'-didecyloxy-4,4'-dihexyloxybenzil (2.00 g, 2.77 mmol) was dissolved in dry dichloromethane (150 mL) and cooled to 0 °C. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.883 g, 0.79 mL, 6.22 mmol) was added with a syringe and the mixture was allowed to stir for 5 minutes. VOF_3 (1.20 g, 9.68 mmol) was then added and the reaction mixture was stirred at room temperature for 60 minutes. The solution was then poured over a citric acid aqueous solution (10 g, 100 mL) and allowed to stir for 15 minutes then poured in a separatory funnel. The organic phase was removed and the aqueous layer was extracted with dichloromethane (75 mL). The organic phases were combined, washed with water (200 mL) and brine (200 mL). The solution was dried over MgSO_4 , filtered and evaporated. The solid obtained was purified over silica (93/7; dichloromethane/hexanes) to remove any remaining starting material. The product was recrystallized in hot hexanes to yield a red solid (1.38 g, 1.91 mmol, 69 %). mp: 80-81 °C; ^1H NMR (500 MHz, CDCl_3) δ 0.87-0.94 (m, 12H), 1.27-1.38 (m, 32H), 1.41-1.56 (m, 8H), 1.81-1.93 (m, 8H), 4.04 (t, 4H, $J = 6.5$ Hz); 4.07 (t, 4H, $J = 6.5$ Hz), 7.10 (s, 2H), 7.52 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 14.01, 14.13, 22.60, 22.70, 25.67, 25.98, 29.04, 29.08, 29.36, 29.38, 29.57, 29.61,

31.55, 31.92, 69.20, 69.58, 107.26, 113.06, 124.55, 131.19, 149.57, 179.25; MALDI-TOF for $[C_{46}H_{72}O_6-H]^+$ calculated (found): 721.54 (721.67); Elemental Analysis (%) for $[C_{46}H_{72}O_6]$ calculated (found): C, 76.62 (76.31); H, 10.06 (10.08).

4,4'-didecyloxy-3,3'-dihexyloxydiphenylacetylene 4-Decyloxy-1-ethynyl-3-hexyloxybenzene (**6b**) (2.26 g, 6.31 mmol), 1-decyloxy-2-hexyloxy-4-iodobenzene (**5b**) (3.49 g, 7.57 mmol) and CuI (0.361 g, 1.89 mmol) were mixed with tetrahydrofuran (100 mL) and (*i*-Pr)₂NH (4 mL) in a 2-necked round-bottom flask (250 mL). Nitrogen was bubbled through the solution for 15 minutes. Pd(PPh₃)₄ (0.365 g, 0.316 mmol) was added and the nitrogen was bubbled for another ten minutes. The solution was heated at reflux 24 hours. The solution was cooled to room temperature and filtered on silica (washed with CH₂Cl₂). The solution was poured in a separatory funnel and the organic phase was washed with HCl (20 %) until the pH of the aqueous phase remained acidic. The organic layer was then washed with water (200 mL) twice, then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was recrystallized with hexanes to afford a beige solid (3.55 g, 5.14 mmol, 82 %). mp: 94-95 °C; ¹H NMR (CDCl₃, 600 MHz) δ 0.87-0.92 (m, 12H), 1.27-1.37 (m, 32H), 1.44-1.50 (m, 8H), 1.79-1.85 (m, 8H), 4.00 (t, 8H, *J* = 6.6 Hz), 6.82 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 2H, *J* = 1.8 Hz), 7.07 (dd, 2H, *J* = 8.4, 1.8 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 14.05, 14.14, 22.64, 22.71, 25.71, 26.02, 29.20, 29.23, 29.36, 29.44, 29.59, 29.63, 31.60, 31.93, 69.16, 69.22, 87.97, 113.28, 115.64, 116.54, 124.73, 148.71, 149.46; MALDI-TOF for $[C_{46}H_{74}O_4-H]^+$ calculated (found): 691.57 (691.56); Elemental Analysis (%) for $[C_{46}H_{74}O_4]$ calculated (found): C, 79.95 (80.12); H, 10.79 (10.67).

4,4'-Didecyloxy-3,3'-dihexyloxybenzil**4,4'-Didecyloxy-3,3'-**

dihexyloxydiphenylacetylene (2.03 g, 2.94 mmol) and I₂ (1.49 g, 5.87 mmol) were dissolved in DMSO (100 mL). The mixture was heated at reflux for three hours and allowed to cool down to room temperature overnight. Water (100 mL) and CH₂Cl₂ (100 mL) were added in order to dissolve the solid formed. The two phases were separated and the organic phase was washed with a Na₂S₂O₃ (200 mL) saturated solution, then with large amounts of water (350 mL) three times, and then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was recrystallized in hot hexanes to yield a white solid (1.96 g, 2.71 mmol, 92 %). mp: 90-91 °C; ¹H NMR (CDCl₃, 600 MHz) δ 0.87-0.92 (m, 12H), 1.26-1.37 (m, 32H), 1.44-1.50 (m, 8H), 1.81-1.86 (m, 8H), 4.04-4.07 (m, 8H), 6.85 (d, 2H, *J* = 8.4 Hz), 7.43 (dd, 2H, *J* = 8.4, 2.4 Hz), 7.56 (d, 2H, *J* = 2.4 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 14.01, 14.10, 22.59, 22.67, 25.63, 25.90, 28.91, 29.00, 29.32, 29.52, 29.56, 31.53, 31.88, 69.10, 69.21, 111.55, 112.23, 126.11, 126.17, 149.27, 154.96, 193.81 (1 carbon signal missing/overlapping); MALDI-TOF for [C₄₆H₇₄O₆-H]⁺ calculated (found): 723.56 (723.57); Elemental Analysis (%) for [C₄₆H₇₄O₆] calculated (found): C, 76.41 (76.51); H, 10.32 (10.32).

3,6-didecyloxy-2,7-dihexyloxyphenanthrene-9,10-dione**4,4'-Didecyloxy-3,3'-**

dihexyloxybenzil (1.31 g, 1.81 mmol) was dissolved in dry CH₂Cl₂ (150 mL) in a two-necked round-bottom flask under nitrogen. The mixture was cooled down in an ice/water bath and BF₃•Et₂O (0.64 g, 4.52 mmol, 0.81 mL) was added with a syringe. The solution was allowed to stir for about ten minutes and VOF₃ (0.78 g, 6.3 mmol) was added. The reaction was allowed to stir at room temperature for 90 minutes. The solution was poured

over a citric acid solution (10 g for 100 mL of water) and stirred for 20 minutes. The two phases were separated and the organic layer was washed with water (2x150 mL) twice, then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was purified on a silica column (100 % DCM) and recrystallized in hot acetone to yield a red solid (0.94 g, 1.30 mmol, 72 %). mp: 79-80 °C ;¹H NMR (CDCl₃, 600 MHz) δ 0.87-0.93 (m, 12H), 1.27-1.42 (m, 32H), 1.48-1.54 (m, 8H), 1.82-1.87 (m, 4H), 1.88-1.92 (m, 4H), 4.07 (t, 4H, *J* = 6.6 Hz), 4.19 (t, 4H, *J* = 6.3 Hz), 7.11 (s, 2H), 7.54 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ 14.01, 14.10, 22.59, 22.68, 25.62, 26.00, 28.97, 29.12, 29.34, 29.39, 29.55, 29.60, 31.52, 31.89, 69.16, 69.55, 107.22, 113.02, 124.51, 131.16, 149.50, 155.58, 179.24; MS-ESI for [C₄₆H₇₂O₆-H]⁺ calculated (found) 721.5 (721.5); Elemental Analysis (%) for [C₄₆H₇₂O₆] calculated (found): C, 76.62 (76.31); H, 10.06 (10.08).

3,4'-Didecyloxy-3',4-dihexyloxydiphenylacetylene (7) 1-Decyloxy-4-ethynyl-2-hexyloxybenzene (2.55 g, 7.10 mmol), 2-decyloxy-1-hexyloxy-4-iodobenzene (3.95 g, 8.58 mmol) and CuI (0.412 g, 2.16 mmol) were mixed in tetrahydrofuran (100 mL) and (*i*-Pr)₂NH (three mL) in a two-necked round-bottom flask (250 mL). Nitrogen was bubbled through the solution for 15 minutes. Pd(PPh₃)₄ (0.410 g, 0.355 mmol) was added and the nitrogen was bubbled for another ten minutes. The solution was heated at reflux for 24 hours. The solution was cooled to room temperature and filtered on silica (washed with CH₂Cl₂). The solution was poured in a separatory funnel and the organic phase was washed with 20 % HCl until the pH of the aqueous phase remained acidic. The organic layer was then washed with water (200 mL) twice, then brine (200 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was recrystallized with hexanes to

afford a beige solid (3.80 g, 5.50 mmol, 77 %). mp: 84-85 °C; ¹H NMR (CDCl₃, 400 MHz) δ 0.87-0.92 (m, 12H), 1.27-1.36 (m, 32H), 1.44-1.50 (m, 8H), 1.79-1.84 (m, 8H), 4.01 (t, 8H, *J* = 4.4 Hz), 6.82 (d, 2H, *J* = 5.6 Hz), 7.02 (d, 2H, *J* = 1.2 Hz), 7.07 (dd, 2H, *J* = 5.6, 1.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 14.02, 14.11, 22.60, 22.61, 22.68, 25.67, 25.68, 26.00, 26.01, 29.16, 29.17, 29.20, 29.22, 29.34, 29.41, 29.57, 29.60, 29.61, 31.58, 31.90, 69.14, 69.19, 87.95, 113.26, 115.61, 116.52, 124.71, 148.69, 149.43 (10 carbon signals missing/overlapping); MS-ESI for [C₄₆H₇₄O₄-H]⁺ calculated (found): 691.6 (691.8); HR-MS for [C₄₆H₇₄O₄-H]⁺ calculated (found): 691.5665 (691.5679).

3,4'-Didecyloxy-3',4-dihexyloxybenzil (8) 3,4'-Didecyloxy-3',4-dihexyloxydiphenylacetylene (7) (3.02 g, 4.38 mmol) and I₂ (2.23 g, 8.79 mmol) were dissolved in DMSO (100 mL). The mixture was heated at reflux for three hours and allowed to cool down to room temperature overnight. Water and CH₂Cl₂ were added in order to dissolve the solid formed. The two phases were separated and the organic phase was washed with a Na₂S₂O₃ (250 mL) saturated solution, then with large amounts of water (350 mL) three times then brine (150 mL). The solution was dried over MgSO₄, filtered and evaporated. The product was recrystallized in hot hexanes to yield a white solid (2.66 g, 3.68 mmol, 84 %). mp: 87-88 °C; ¹H NMR (CDCl₃, 400 MHz) δ 0.87-0.92 (m, 12H), 1.27-1.38 (m, 32H), 1.44-1.50 (m, 8H), 1.81-1.87 (m, 8H), 4.04-4.07 (m, 8H), 6.85 (d, 2H, *J* = 5.6 Hz), 7.43 (dd, 2H, *J* = 5.6, 1.2 Hz), 7.56 (d, 2H, *J* = 1.2 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 13.98, 14.01, 14.10, 14.11, 22.56, 22.60, 22.67, 22.68, 25.57, 25.64, 25.91, 25.98, 28.86, 28.91, 29.01, 29.06, 29.32, 29.34, 29.38, 29.53, 29.56, 29.60, 31.49, 31.54, 31.88, 31.90, 69.10, 69.21, 111.55, 112.22, 112.24, 126.12, 126.17, 149.27,

149.28, 154.96, 193.81 (9 carbon signals missing/overlapping); MS-ESI for $[C_{46}H_{74}O_6-H]^+$ calculated (found): 723.6 (723.0); HR-MS for $[C_{46}H_{74}O_6-H]^+$ calculated (found): 723.5564 (723.5574).

2,6-Didecyloxy-3,7-dihexyloxyphenanthrene-9,10-dione (9) 3,4'-Didecyloxy-3',4'-dihexyloxybenzil (**8**) (2.24 g, 3.10 mmol) was dissolved in dry CH_2Cl_2 (200 mL) in a two-necked round-bottom flask under nitrogen. The mixture was cooled down in an ice/water bath and $BF_3 \cdot Et_2O$ (1.10 g, 7.75 mmol, 1.4 mL) was added with a syringe. The solution was allowed to stir for about ten minutes and VOF_3 (1.44 g, 11.6 mmol) was added. The reaction was allowed to stir at room temperature for 90 minutes. The solution was poured over a citric acid solution (10 g for 100 mL of water) and stirred for 20 minutes. The two phases were separated and the organic layer was washed with water (150 mL) twice then brine (150 mL). The solution was dried over $MgSO_4$, filtered and evaporated. The solid was purified on a silica column (100 % DCM) and recrystallized in hot acetone to yield a red solid (1.75 g, 2.43 mmol, 79 %). mp: 69-70 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 0.87-0.89 (m, 6H), 0.90-0.94 (m, 6H), 1.28-1.41 (m, 32H), 1.48-1.55 (m, 8H), 1.82-1.87 (m, 4H), 1.88-1.92 (m, 4H), 4.05-4.08 (m, 4H), 4.17-4.20 (m, 4H), 7.10 (s, 2H), 7.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.00, 14.10, 22.58, 22.67, 25.62, 25.65, 25.96, 26.00, 28.97, 29.02, 29.06, 29.12, 29.33, 29.37, 29.39, 29.55, 29.59, 29.60, 31.52, 31.53, 31.89, 69.15, 69.54, 107.20, 112.99, 124.49, 131.14, 149.49, 155.57, 179.22 (note: 9 carbon signals missing/overlapping); MS-ESI for $[C_{46}H_{72}O_6-H]^+$ calculated (found): 721.5407 (721.5432); HR-MS for $[C_{46}H_{72}O_6-H]^+$ calculated (found): 721.5407 (721.5398).

General procedure for the preparation of tetraalkoxydibenzo[*f,h*]quinoxaline-2,3-dicarbonitrile (BQ): 2,3,6,7-Tetraalkoxyphenanthrene-9,10-dione and diaminomaleonitrile were mixed in acetic acid (25 mL) and nitrogen was bubbled for 15 minutes. The mixture was heated at reflux for 24 hours and then cooled down to room temperature. The solution was poured over ice, water was added and the solution was stirred until the ice was melted. The aqueous solution was extracted with CHCl₃ (50 mL) three times and the layers were combined. The organic phase was washed with water (50 mL) twice, then with brine (75 mL). The solution was dried over MgSO₄, filtered and evaporated. The solid was purified on a short silica column (CH₂Cl₂) and TLC showed the presence of only one product. The solid was recrystallized from hot acetone to yield an orange solid. Amounts used are specified below for each compound.

BQ(10,6,6,10): 6,11-Didecyloxy-7,10-dihexyloxydibenzo[*f,h*]quinoxaline2,3-dicarbonitrile 2,7-Didecyloxy-3,6-dihexyloxyphenanthrene-9,10-dione: 0.122 g, 0.169 mmol; diaminomaleonitrile: 0.183 g, 1.69 mmol; Final product: 0.0401 g, 0.0506 mmol, 30 %; ¹H NMR (CDCl₃, 600 MHz) δ 0.88 (t, 6H, *J* = 6.8 Hz), 0.94 (t, 6H, *J* = 7 Hz), 1.25-1.46 (m, 24H), 1.55-1.63 (m, 16H), 1.94-2.02 (m, 8H), 4.26 (t, 4H, *J* = 6.5 Hz), 4.30 (t, 4H, *J* = 6.5 Hz), 7.66 (s, 2H), 8.40 (s, 2H) ¹³C NMR (CDCl₃, 150 MHz) δ 14.05, 14.14, 22.65, 22.72, 25.79, 26.13, 29.14, 29.16, 29.40, 29.61, 29.67, 31.63, 31.94, 69.29, 69.51, 105.06, 107.92, 114.45, 120.99, 128.03, 128.28, 141.16, 150.07, 153.81; MALDI-TOF for [C₅₀H₇₂N₄O₄-H]⁺ calculated (found): 793.56 (793.28); Elemental Analysis (%) for [C₅₀H₇₂N₄O₄] calculated (found): C, 75.72 (75.28); H, 9.15 (9.17); N, 7.06 (6.68).

BQ(6,10,10,6) (7,10-Didecyloxy-6,11-dihexyloxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile) 3,6-Didecyloxy-2,7-dihexyloxyphenanthrene-9,10-dione: 0.118 g, 0.164 mmol; diaminomaleonitrile: 0.177 g, 1.64 mmol; Final product: 0.0490 g, 0.0618 mmol, 38 %; ¹H NMR (CDCl₃, 600 MHz) δ 0.89 (t, 6H, *J* = 6.9 Hz), 0.95 (t, 6H, *J* = 6.9 Hz), 1.25-1.47 (m, 32H), 1.58-1.62 (m, 8H), 1.95-2.02 (m, 8H), 4.22 (t, 4H, *J* = 6.6 Hz), 4.28 (t, 4H, *J* = 6.3 Hz), 7.58 (s, 2H), 8.28 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ 14.04, 14.11, 22.64, 22.69, 25.77, 26.14, 29.09, 29.20, 29.37, 29.50, 29.60, 29.66, 31.64, 31.92, 69.22, 69.41, 104.80, 107.69, 114.40, 120.77, 127.89, 128.07, 140.86, 149.91, 153.70; MS-ESI for [C₅₀H₇₂N₄O₄-Na]⁺ calculated (found): 815.5 (815.2); Elemental Analysis (%) for [C₅₀H₇₂N₄O₄] calculated (found): C, 75.72 (75.89); H, 9.15 (9.28); N, 7.06 (6.85);

BQ(6,10,6,10) (6,10-Didecyloxy-7,11-dihexyloxydibenzo[f,h]quinoxaline-2,3-dicarbonitrile) 2,6-Didecyloxy-3,7-dihexyloxyphenanthrene-9,10-dione (**9**): 0.1248 g, 0.173 mmol; diaminomaleonitrile: 0.187 g, 1.73 mmol; Final compound: 0.0169 g, 0.021 mmol, 12 %; ¹H NMR (CDCl₃, 600 MHz) δ 0.89 (t, 6 H, *J* = 7.2 Hz), 0.95 (t, 6 H, *J* = 7.2 Hz), 1.25-1.46 (m, 32H), 1.57-1.62 (m, 8H), 1.95-2.02 (m, 8H), 4.23-4.25 (m, 4H), 4.30 (t, 4H, *J* = 6.6 Hz), 7.63 (s, 2H), 8.35 (s, 2H); ¹³C NMR (CDCl₃, 150 MHz) δ 14.03, 14.11, 22.64, 22.69, 25.76, 25.78, 26.11, 26.12, 29.08, 29.13, 29.15, 29.19, 29.365, 29.374, 29.48, 29.59, 29.65, 30.93, 31.62, 31.91, 69.25, 69.45, 104.93, 107.80, 114.41, 120.88, 127.95, 128.17, 141.01, 149.98, 149.99, 153.75 (18 carbon signals missing/overlapping); MS-ESI for [C₄₉H₆₈N₄O₄]⁺ calculated (found): 776.5241 (776.2273); Elemental Analysis (%) for [C₅₀H₇₂N₄O₄] calculated (found): C, 75.72 (75.73); H, 9.15 (9.16); N, 7.06 (6.73).

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